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(54) METHOD OF PRODUCING TITANIUM DIOXIDE

There is a known method for producing titanium dioxide by oxidizing titanium tetrachloride in oxygen-containing plasma. In this case, oxygen is heated in a high-frequency gas discharge. However, this method is complicated due to the complex system for creating an oxygen-containing plasma.

In order to simplify the process, it is proposed to heat the oxygen-containing gas in a stabilized electric arc.

Atmospheric air with the dust removed is used as the plasma-forming gas. The air plasma is produced in electric arc heaters. To improve the mixing, three plasma jets are introduced into the reaction zone such that the jets form a plasma funnel, into which is introduced finely atomized liquid TiCl_4 . The reacting flow at speed of 700 m/s passes through a quenching nozzle into a cooled volume. From the cooled volume, the dust-containing mixture is directed to a system for trapping the TiO_2 .

Tests are conducted with 20% oxygen excess, temperature of the air plasma at the entry to the reaction zone 3000-3200°K; temperature in the reaction zone 2200-2300°K; dwell time for the reagents in the reaction zone $2-20 \cdot 10^{-3}$ s; outlay of electricity 2-3 kWh/kg of TiO_2 . The resulting titanium dioxide contains 87-97% rutile without introduction of rutilizing additives, the TiO_2 particle diameter is 0.1-0.4 μ ; the particle shape is spherical and oval (electron microscope analysis).

The chlorine gas leaving the titanium dioxide trapping system contains around 25 vol. % of chlorine. The chlorine gas is used to produce chlorine derivatives. A mixture of oxygen and air (70% oxygen, 30% air) is used as the plasma-forming gas, which makes it possible to reduce the outlay of energy for production of titanium dioxide to 1.3-1.5 kWh/kg of TiO_2 and obtain concentrated chlorine gas (chlorine content around 70 vol. %). Such chlorine gas can be used for chlorination of titanium-containing raw material.

Patent claim

Method of production of titanium dioxide by oxidizing titanium tetrachloride in oxygen-containing plasma, characterized in that, to simplify the process, the oxygen-containing gas is heated in a stabilized electric arc.

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PATENT APPLICATION

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(54) **Method of production of powders of ceramic, metallic or similar products by plasma arc.**

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The present invention concerns an electrothermal method of preparation of powders of carbides or of nitrides or metallo-ceramics (cermet) in a plasma arc furnace, having an anode function without dissipative cooling.

It is known that, under identical conditions of energy content (enthalpy), a plasma produced by a gas which is monoatomic under normal conditions (rare or noble gas) is at a temperature which is far higher than that of a plasma produced by a gas consisting of diatomic molecules (ordinary gases). In fact, at 80 kcal/mole, the mean temperature of hydrogen plasma is 3880°K, whereas the mean temperature of argon plasma is 11,000°K.

In plasma generating devices with nonconsuming electrodes, continuous duty is made possible by a powerful cooling applied to the electrodes themselves. In direct current arc devices, the positive electrode, or anode, is the one that receives the beam of electrodes of the plasma arc; by reason of the very high temperature developed, the latter is responsible for very high energy density values being found in the anode zone. In order to prevent fusion, especially of the anode, strong cooling is provided, for example, by means of a forced refrigeration circuit, most of the time using water.

This necessity is responsible for energy losses in the plasma generators which may reach 50% or more in the case of rare gas plasma, and 25% or more in the case of ordinary gas plasma, in terms of the total energy applied to the plasma arc.

Because of the phenomenon of atom reassociation which regenerates the initial molecules, the plasmas of nonrare gases offer a longer thermally useful lifetime, while on the other hand the rare gas plasmas, for the opposite reason, present a faster thermal decline.

For applications to chemical reactions, where the reaction power requires the supplying of heat and elevated temperatures, there is particular interest in plasmas of ordinary gases. More specifically, hydrogen plasmas have been tested out and utilized in systems where, besides lower energy losses and the slower decline in the thermal level, it is of interest to utilize the reducing properties of hydrogen with regard to the reacting substances, as in the case of the reaction between TiCl_4 and a halogenated hydrocarbon, such as CCl_4 , to obtain TiC .

In these processes thus far, efforts to make use of graphite anodes have failed since, in argon plasmas, the high temperature in the impact zone of the plasma arc produces a vaporization of the graphite, while in hydrogen plasmas there is a chemical corrosion of the graphite due to the formation of hydrocarbons.

Consequently, the plasma reactor generally used is a hydrogen plasma reactor with metal electrodes protected by a forced water cooling circuit.

In the case of products which are more difficult to obtain in thermodynamic respect, such as TiC , the conversion of the reacting substances may be slight, with an elevated specified consumption of the plasma-producing gas, as well as of the electrical energy necessary for the plasma arc, per each kilogram of product produced.

Furthermore, the prior methods are characterized by a slight concentration of the total volume of reacting substances in terms of the total volume of the gas system (plasma forming gas + gas of the injected reacting substances).

Thus, the purpose of the invention is to propose an improved electrothermal method which eliminates the drawbacks and the limitations of the prior methods.

This result is achieved thanks to the fact that the carbides prepared in an argon plasma are economically more advantageous and have better characteristics of resistance to oxidation at high temperature than the carbides prepared in a hydrogen plasma.

Furthermore, it has been noticed that it was not only possible to use graphite for the main anode, without the latter undergoing wear by vaporization or sublimation in an argon plasma, but also that, despite the very high temperature of the argon plasma, it was possible to use not only graphite anodes but also noncooled tungsten anodes, without the latter undergoing damage.

All these advantages are obtained in practice by a plasma arc method for the production of powders of various chemical products, by endothermal reactions, this method consisting, according to the invention, in realizing in a furnace with an anode function without dissipative cooling, and in continuous operation, the following operational phases, which consist in:

a) forming a chemically reactive fluid dynamic mass with a high caloric content and an elevated concentration of reacting substances, by injecting into the electron plasma arc a rare gas, one or more halides of one or more metals or one or more metallides, which pass through a mix injection throttling nozzle arranged in a state of electrical insulation;

b) condensing this fluid dynamic mass in a primary anode in the shape of a nozzle without a dissipative or forced cooling system; and finally

c) injecting into this mass (electronically condensed) the remainder of one or more reacting substances needed to accomplish the particular chemical reaction.

The method according to the invention makes it possible to obtain the aforesaid positive results thanks to the fact that hydrogen, as the plasma-forming gas, is replaced by a rare gas such as argon or helium, preferably argon, and at the same time thanks to the use of a furnace with an anode function of the type specified in Italian patent application No. 20242 of 02.17.1976 for "Plasma arc furnace with anode function without dissipative cooling, as a chemical reactor for high temperatures", in which it is even possible to use graphite as the anode material to support the electronic condensation of the plasma arc.

As a variant, it is possible to use a refractory metal such as tungsten, although it will generally be preferable to use graphite under the operating conditions of the method according to the invention.

The advantages of the method according to the invention are obtained by working so as to achieve, in a first phase, an elevated heat level and a high concentration of the reactive substances of a reactant, by injecting one or more halides of metals or of metallides into the rare gas plasma, so as to produce a chemically reactive fluid dynamic mass. In a second phase, after having accomplished the corresponding

electronic condensation of the arc inside a primary anode in the form of a nozzle, one or more reactants are injected onto this mass to achieve the particular chemical reaction.

In practice, the method is implemented in absence of hydrogen not required by the stoichiometry of the particular chemical reaction and in presence of limited quantities of a rare gas, so that the starting concentration of the reactants, that is, with a reaction not yet finished and in the cold state, as compared to the total gas system (plasma gas and cooling gas), is equal to or greater than 20% by volume.

The possible reactant hydrogen can be introduced at any rate beneath the anode zone where the condensation of the electronic discharge of the plasma arc occurs.

The advantages of this method over the prior methods are:

- larger conversion rates of the reacting substances;
- less thermal dispersion and, consequently, a higher energy efficiency, which means a lower energy consumption per kilogram of product obtained;
- higher production;
- lower consumption of the gas forming the plasma per unit quantity of product obtained;
- better granulometric characteristics of the powders thus produced;
- lower ratio between the gas used to form the plasma and the power applied to the arc;
- longer longevity of the cathode, due to the fact it is maintained solely in an argon atmosphere.

Other characteristics and advantages of the invention will appear in the course of the following description.

On the enclosed drawing, given solely as an example and in no way limiting, the single figure is an axial section through an apparatus which is particularly useful for implementing the method according to the invention.

The apparatus shown is not the subject of the invention, since it consists of a classical hydrogen plasma arc apparatus combined in series with an improved furnace, of a type already known.

In the drawing, the classical plasma generator is represented by the part indicated as A, whereas the plasma arc furnace mentioned above comprises the assemblage of parts indicated as B, C, D.

The plasma generator thus contains a cathode section 1 provided with a cooling device comprising an annular cavity with an inlet 2 and an outlet 3 for the cooling water; an interchangeable tungsten cathode 4, secured in an electrically insulating tubular element 5; an anode section 6 with a water cooling device similar to that of the cathode compartment; an interchangeable copper anode nozzle 7; a chamber 8 for generating a plasma arc and for blowing with an inlet 9 for the gas producing the plasma.

All the elements 1-9 are enclosed between a support bearing 10 provided with a cooling system 11 and the opposite connection plate 12; these elements are arranged between an electrical insulating disk 13 and a connection and sealing ring 14, likewise insulating.

In practice, the assemblage of part A is located between the plate 13 and the insulating ring 14. The support bearing 10, comprising an annular cavity 11 for the cooling water, forms the connection

element to the furnace and its anode function which, as has already been mentioned above, comprises all the parts designated as B, C, D.

This furnace comprises, in part B, a throttle nozzle 15 for injection and mixing of the electron column of the plasma arc, made of graphite and electrically insulated. The furnace is provided with a first series of injection nozzles 16, arranged tangentially so as to produce a vortex, and connected to a distribution cavity 17; and a second series of nozzles 18, likewise arranged tangentially and connected to a feed cavity 19, like cavity 17, for introducing reactive plasmogenic gas, whether or not added to one or more reacting substances.

A graphite cylinder 20 plays the part of a screen for the nozzle 15.

The primary anode head, or part C, is enclosed between two insulating rings 21 and 22 and it is supported by a bottom bearing 23 comprising an annular cooling cavity and two inlets 24 and 25 for one or more reacting substances. On the bearing 23 is secured an anode tube 26 of graphite with two holes or channels 27 and 28 for introduction of the injected material, these channels being respectively connected to the inlets 24 and 25. At the end of the anode tube 27 there is screwed on a primary tungsten anode 29, provided with a first injection nozzle 30 fed by the lengthwise inlet channel 25, and a second nozzle 31, fed by the channel 24. Furthermore, there is provided a radial injection nozzle 30'.

The anode tube 26 and the corresponding anode 29 are enclosed between two cylindrical metal sleeves 32 and 33, whose air volume forms a cylindrical cavity cooled by water; the anode tube 26 is surrounded by a graphite cylinder 34, playing the part of a screen, while the air volume or cavity between the cylinder 34 and the sleeve 32 is filled with a spongy graphitized insulating or nonconducting material of carbon black [or?] of graphite wool.

Reference 35 designates the entrance of the reactive gas producing the plasma, with or without one or more reacting substances added, directed toward the furnace.

The end section of the furnace, or section D, consists of a cylindrical body 36 closed on top by a bearing 37 which contains a cooling system with two inlets 38 and 39 for the reacting substances or for the materials injected into the center of the furnace, and at the bottom by a sealing collar 40 provided with a water cooling device. At the center of the body 36 there is arranged a graphite tube 41 with an upper insulating graphite ring 42, of such shape that it constitutes nozzles used to inject the reacting substances or the materials brought up by the conduits 38 and 39 into the tube 41.

A graphite cylinder 43 plays the part of a screen, while an insulating material 44 is inserted between the inner surface of the cylindrical body 36 and the cylinder 43.

Finally, the apparatus has electrical power supply connections, comprising a cathode conductor 45, a direct current feed conductor 46, an anode conductor 47, an auxiliary switch 48, an auxiliary anode pilot conductor 49 and an electromagnetic field winding 50.

A condition of particular efficiency and resistance of this furnace is achieved when the gases which are introduced into the plasma by the throttle nozzle 15 undergo a strong rotation, and/or when the last portion of the plasma arc column is radially deformed or twisted.

Another favorable condition is obtained by rotating the plasma arc relative to the surface of the anode tube 26 on which the discharge is condensed; this rotation can be achieved by applying a magnetic field. This magnetic field can be developed the same way as in the prior art, or produced automatically by the anode current itself in the winding 50.

This furnace represents a plasma arc device in which a tube with an anode function 26 is used under conditions of insulation.

The tube 26 with an anode function supports an anode 29, on whose nozzle the plasma arc is electronically condensed.

The method according to the invention essentially consists in producing, upstream from the anode 29, which is not cooled and which can be made of tungsten or graphite, a chemically reactive fluid dynamic mass with an elevated heat content and a high concentration of reacting substances.

This mass is obtained by injecting, into the plasma of rare gas (argon), one or more reacting substances consisting of one or more halides of metal or of metallide. The rare gas plasma is initially produced by a classical plasma generator consisting of the elements designated as 1-9 in section A of the drawing.

The chemically reactive fluid dynamic mass is produced by the aforesaid injection, which is accomplished and controlled by the section B, which comprises the throttling, injecting and mixing nozzle 15; section B plays the triple role of throttling the plasma arc in the nozzle 15, injecting into it by the tangential injection nozzles 16 and 18 one or more reacting substances preferably consisting of halides of metals or of metallides, and imposing on them a mixing effect by vortex, thanks to the vortex motion imparted to the reacting substances by the tangential injection with the nozzles 16 and 18.

The injection of the first type of reacting substance, especially the halides, makes it possible to excite the plasma arc with a very large value of voltage absorption, among other things.

In fact, it is known that, for a given electric current strength, argon plasma produces a low voltage drop with resulting limitation on the value of the electric power involved in the arc. Consequently, the fluid dynamic mass thus formed and excited has an elevated caloric content and a high concentration of reacting substances after the increased exchange of impacts occurring between the column of electrons of the arc and the chemical substances that are injected into it. At the same time, the rare gas, preferably argon, guides and stabilizes the plasma arc itself.

Inside the nozzle of the primary anode 29, the electrons of the arc current situated inside the chemically reactive fluid dynamic mass are themselves condensed, thus closing the power supply circuit of the plasma arc. In the lower portion of the anode 29, through the radial injection nozzle 30' and through the inclined nozzles 30 and 31, one or more reacting substances of the second type, such as CH_4 , H_2 , NH_3 , etc., can be injected, as required by the stoichiometry of the primary reaction, in order to distinguish it from other actions which might be superimposed on it.

At the fluid dynamic mass, lacking the electrons of the electric current which have been absorbed by the anode condensation, the reacting substances of the second type, thanks to the high caloric content

and the elevated concentration of activated chemical substances, encounter reaction conditions with regard to the thermodynamic aspects, as well as the kinematic aspects.

The nozzles 30 and 31 are used to inject, as already mentioned above, the second type of reacting substances, such as H_2 , NH_3 , etc., which it is advantageous to preheat in the inlet channels 27 and 28 of the anode tube 26 for the chemical reaction which is to be produced.

On the other hand, the radial nozzle 30' is used when one or more reacting substances of the second type, such as CH_4 , C_2H_2 , $Ni(CO)_4$, etc., require only slight preheating, so as to prevent these substances from decomposing before coming into contact, and therefore reacting with, the chemically reactive fluid dynamic mass.

Of course, the primary anode 29 can have different shapes and can be made of graphite and/or of tungsten, although graphite is the preferable material.

Moreover, the process described above is characterized not only by absence of hydrogen which is not required by the stoichiometry of the particular chemical reaction, but also by a limited quantity of rare gases as compared to the quantity of reacting substances, so that the initial concentration of the latter, considered in the state of the still unfinished reaction and the cold state, is at least 20% by volume of the total gas system, namely, the plasma gas with the reacting substances of the first type and the reacting substances of the second type.

If the primary reaction requires hydrogen as a reacting substance, the latter is injected in any given way beneath the anode zone where the condensation of the electron discharge of the plasma arc occurs.

The method according to the invention offers the major advantage of a stronger concentration of reacting substances, more than 20% by volume, in terms of the total gas system, namely, the plasma gas, the reacting substances of the first type and the reacting substances of the second type.

The excitation of the rare gas plasma arc can also be accomplished by injecting into the plasma one or more reacting substances of the second type, such as CH_4 , C_2H_2 , NH_3 , etc., but the fluid dynamic mass thus obtained has a weaker power of chemical reaction, with other drawbacks such as easy clogging of the nozzles of the primary anode.

Consequently, the excitation of the rare gas plasma arc is done preferably by injecting into it one or more reacting substances of the first type, or halides of one or more metals and/or one or more metallides.

Preferably, the method according to the invention is put into effect by using a tubular anode support 26 of graphite and a primary anode 29, likewise of graphite, provided with injection nozzles 30' and/or 30 and 31.

The injection nozzles make it possible to introduce, with the gaseous or evaporable reacting substances, one or more fine powdered solid substances, in order to achieve one of the two purposes mentioned hereafter.

The first of these purposes is to utilize the powder injected as a nucleation agent and as growth seeds to accomplish, for example, powders with larger granular dimension. In this case, the powder injected

is chemically identical to the powder produced by the primary reaction. This technique offers the possibility of determining the granulometry of the powders, for example, carbides or nitrides of metals such as TiC, Si_3N_4 , B, etc.

The second purpose is to utilize the powder injected as a dispersal agent in relation to the powder produced by the primary reaction. In this case, the powder or powders injected are chemically different from those produced by the primary reaction. It is thus possible to obtain cermet compositions in which one phase differs from a second phase, such as TiC-Ni.

Obviously, other series of injectors 30', 30 and 31 can be placed at an intermediate height of the anode tube 26 in such cases where this is necessary because of the type of powder injected.

Furthermore, the method according to the invention makes it possible to use the powder produced by the primary chemical reaction as a germination and growth nucleus for the composite material, if said powder is subjected to a following reaction.

This following reaction can be developed by a chemical and/or physical reaction of one or more reacting substances introduced into a zone of the furnace situated beneath that where the primary reaction occurs.

The reacting substances required for the following reaction are introduced, alone or in mixture, by the conduits 38 and 39, communicating respectively with the injection nozzles arranged in appropriate fashion in the graphite ring 42.

The method according to the invention is especially suitable for high-temperature endothermal reactions, such as those involved in the production of:

- ceramic carbides, such as: TiC, SiC, Cr_3C_2 , B_4C , TaC, WC, MoC, NbC, etc.;
- mixed ceramic carbides, such as: WC-MoC, WC-TaC, WC-TaC-MoC, etc.;
- ceramic nitrides, such as: Si_3N_4 , TiN, etc.;
- metal borides, such as: TiB_2 , ZrB, CrB, etc.;
- metals, such as: B, Ni, Mo, Cr, Ti, Si, etc.;
- metal chlorides, such as: TiCl_3 , by partial reduction of TiCl_4 ;
- intermetallic products, such as: Si-Mo;
- cermets, such as: metal-carbide-ceramic;
- composite products, such as: Si_3N_4 - nickel;
- organic products, such as acetylene;
- inorganic products, such as hydrocyanic acid.

The products which can be obtained by this method, even in the state of powders with size less than a micron, are not pyrophoric.

Six examples shall be given hereafter, as nonlimiting illustration, namely, the first one according to the prior art, and the second one already described elsewhere with regard to a furnace having an anode function.

Example 1:

This example concerns the preparation of TiC from TiCl_4 and CH_4 in a hydrogen plasma according to known method and equipment, more precisely, in the apparatus represented by portion A of the drawing, in which two nozzles are provided for injecting the reacting substances, one in the anode nozzle 7 and one radially beneath the anode 7. This example was considered in two trials whose operating conditions were as follows:

In the first case:

Electric current strength	115 amperes
Total electric power	11.5 kW
Arc voltage	100 volts
Rate of introduction of the arc gas (hydrogen)	1500 NI/h
Plasma temperature at exit from the anode 7	3300°C
Distance between the injector and the front of the anode 7:	1.5 cm
Gas mixture introduced into the injector of the anode 7:	
TiCl_4	0.36 kg/h (equal to 42.5 NI/h)
CH_4	84.0 NI/h (equal to 0.06 kg/h)
Molecular ratio $\text{TiCl}_4/\text{CH}_4$	≈ 0.50
Resulting product TiC	0.102 kg/h
Theoretical conversion with respect to TiCl_4	89.6%
Theoretical conversion with respect to CH_4	45.5%
Concentration of reacting substances ($\text{TiCl}_4 + \text{CH}_4$) in the injected plasma ($\text{H}_2 + \text{TiCl}_4 + \text{CH}_4$):	
$\frac{42.5 + 84}{42.5 + 84 + 1500} \cdot 100 =$	7.8% by volume
Energy consumption (kWh) per kg of TiC	112.8 kWh/kg

In the second case:

Total power	45 kW
Gas (hydrogen) supply	11,760 NI/h
Reacting substances injected:	
TiCl_4	8.64 kg/h (equal to 1020 NI/h)
CH_4	1020 NI/h (equal to 0.728 kg/h)
Molecular ratio $\text{TiCl}_4/\text{CH}_4$	1.0

Concentration of reacting substances
($\text{TiCl}_4 + \text{CH}_4$) in the injected plasma
($\text{H}_2 + \text{TiCl}_4 + \text{CH}_4$):

$$\frac{1020 + 1020}{1020 + 1020 + 11760} \cdot 100 = 14.8\% \text{ by volume}$$

Theoretical conversion (with respect to TiCl_4
and CH_4) 51%

Hourly efficiency in TiC 1.39 kg/h

Energy consumption (kWh) per kg of TiC 32.3 kWh/kg
N1 = liters under normal conditions.

Example 2:

This involves the preparation of TiC from TiCl_4 and CH_4 injected into a hydrogen plasma (83.5% by volume with 16.5% by volume of argon), making use of equipment from the above-cited application.

In this case, an anode prepared as follows was used. A cylindrical core of graphite with two diameters and two heights ($\varnothing = 18$ and $h = 56$ mm; $\varnothing = 12$, $h = 7$ mm) was covered by a plasma sputtering method with a layer of tungsten whose outer surface was ground to $\varnothing = 22$ mm for the entire height. The graphite core was perforated at $\varnothing = 15$ mm over a height of $h = 56$ mm and at $\varnothing = 9$ mm for $h = 7$ mm. This made it possible to obtain a primary anode of composite type, consisting of tungsten completely covered with a layer of graphite having a thickness of 1.5 mm.

This anode was screwed and locked to a graphite support 26; the latter was flat in form with a minimum thickness of 7 mm and a diameter of 20 mm, having transferred to this support the injection holes 30 and 31 from the initial position to the lower portion of the primary anode 29. The new holes 30, 31 in their new position relative to the figure made an angle of 45° relative to the furnace axis, communicating with the inlets 24, 25 by the channels 27, 28.

The coil 50 is of customary type, being excited by alternating current, and its number of turns is such that it develops a magnetic field of 1000 gauss.

The connection to the positive pole of the electrical current generator 46 was made by closing the switch 48 and disconnecting the conductor 47 from the collar 37.

The primary anode head 29 was placed at a distance of around 25 mm from the front of the auxiliary or pilot anode nozzle 7, the throttling mixer 15 being made of graphite with a minimum diameter $\varnothing = 10$ mm and the cylindrical end piece forming a screen arranged to cover around three-fourths of the height of the primary anode 29.

This yields a base for the furnace body with an inner graphite tube 41 having an internal diameter of 50 mm and a height of 500 mm.

This is followed by a filter of fabric type, heat-resistant, and by a hydrochloric acid precipitation system for the gases in alkaline solution. The operating conditions were as follows in this case:

Total current strength (at the main arc and at the pilot arc) 95 amperes

Current strength at the pilot arc in the resistant circuit 10 amperes

Arc voltage	158 volts
Total rated capacity (total power)	15 kW
Arc gas feed rate:	
Argon introduced through the classical head inlet	1300 NI/h
Hydrogen introduced through the inlet 17	6600 NI/h

The hydrogen supply was via the distribution cavity 17 and the series of injectors 16 which were tangentially arranged so as to produce a swirling of the hydrogen.

Supply of reacting substances:

TiCl ₄ by the inlet 25	1.587 kg/h
CH ₄ by the inlet 24	178 NI/h
Molecular ratio TiCl ₄ /CH ₄	1.0
Hourly yield of TiC	0.472 kg/h
Theoretical conversion with respect to TiCl ₄ and CH ₄	98.8%
Energy consumption (kWh) per kg of TiC	31.8 kWh/kg
Concentration of reacting substances (TiCl ₄ + CH ₄) in the injected plasma (A + H ₂ + TiCl ₄ + CH ₄):	
$\frac{178 + 178}{178 + 178 + 1300 + 6600} \cdot 100 =$	4.3%

The trial lasted two hours and 55 minutes from the igniting of the plasma arc. The reacting substances were injected into the furnace after a period of 30 minutes, intended to preheat the furnace with the plasma arc in operation.

For the last 35 minutes, the feeding of reacting substances was interrupted and, consequently, the duration of the reaction between the injected reacting substances was one hour and 50 minutes. At the end of the trial, the electrodes were inspected. The cathode was perfectly preserved. The primary anode had lost around 80% by weight of the 1.5 mm graphite thickness used as inner coating of the tungsten anode. Only the lower portion where the anode 29 is locked to the graphite support 26 had preserved the initial graphite coating of 1.5 mm.

The strong irradiation caused by the electronic condensation of the plasma arc in presence of atomic and ionic hydrogen should be doubly considered as causing the chemical corrosion of the graphite with the formation of hydrocarbons.

As for the metallic tungsten of the primary anode, it was observed on the contrary that it had not undergone any alteration and that it was not damaged, even though being exposed to particularly severe operating conditions in the absence of the reacting substances (which, due to the endothermal nature of the reaction, results in not inconsiderable subtraction of heat), both in the initial phase and the end phase.

The auxiliary or pilot anode 7 was perfectly preserved.

No corrosion phenomenon was observed in regard to the graphite pieces, corresponding to elements 26, 42 and 41.

The TiC thus obtained was examined by X-ray and this analysis revealed only the typical peaks of cubic TiC.

Example 3:

This involves the preparation of TiC from TiCl_4 and CH_4 in a plasma lacking direct supply of hydrogen that is not part of the stoichiometric reaction. This preparation is done with the same equipment as that described in example 2, in which the primary anode has been replaced by a new anode of the same dimensions and the same structural characteristics. The operating behavior of the equipment was characterized by the fact that the inlet 18 and the series of tangential injection nozzles 16 were given methane instead of hydrogen, the latter having been completely eliminated from the process. On the other hand, for TiCl_4 , the supply circuit through inlet 25 was maintained unchanged.

In other respects, the trial was carried out in a way similar to that described for example 2.

No corrosion phenomenon was detected in any portion of the equipment. Not even the 1.5 mm graphite lining of the inner cylindrical wall of the primary anode was altered, unlike what occurred in example 2.

This shows that, in absence of hydrogen and using a rare gas such as argon as the nonreacting gas (in the case of the reaction to prepare TiC), it appears that the electrodes, including the primary anode 29, are perfectly preserved, even though the quantity of rare gas used for the plasma arc is extremely slight (namely, $0.087 \text{ Nm}^3/\text{kWh}$).

The TiC thus obtained was examined by X-ray and this test found only the typical peaks of cubic TiC alone.

Example 4:

Thermo-gravimetric tests were carried out in classical furnaces of the Tamman type on the TiC obtained in examples 2 and 3, as well as the product obtained by the carbo-thermal method ($\text{TiO}_2 + 2\text{C} \rightarrow \text{TiC} + \text{CO}$) in order to examine the degree of resistance to thermal oxidation and to relate this to the method of preparation used.

The results obtained are given in table 1. They show that the TiC powder with size less than one micron, prepared with the plasma method in absence of hydrogen, and with the described reactor, has a noteworthy resistance, equal to that of the crude product obtained by the carbo-thermal method, and a much higher resistance than that of the powder of same size, obtained with the method of plasma in hydrogen.

Given that it is very important to obtain a product with a very fine granulometry and also that this product should have good resistance to thermal oxidation, it is clear that the product obtained by the method of plasma without hydrogen constitutes an interesting innovation with regard to the prior art.

Example 5:

This involves the preparation of TiC from TiCl_4 and CH_4 in a plasma lacking any sort of direct supply of hydrogen not part of the stoichiometry of the reaction. This preparation was carried out with the same equipment as that described in example 2. In the present example, the only variant is that the TiCl_4 and CH_4 inlets are switched around.

More specifically, TiCl_4 was introduced through the distribution cavity 17 and the series of tangential injectors 16, so as to impart a vortex motion in the zone of emission of the argon plasma.

The CH_4 was introduced via the inlet 25, the channel 27 and the nozzle 30, arranged as in example 2. Like the product of example 3, the TiC obtained proves to be pure upon X-ray examination, while having a granulometry less than one micron.

Example 6:

This involves the preparation of TiC from TiCl_4 and CH_4 in a plasma lacking any direct supply of hydrogen not part of the stoichiometry of the reaction. This preparation was carried out with the equipment as described for the enclosed drawing.

This equipment differs from that used in example 2, 3, 4 and 5 in that an anode on a tubular support with a height of 370 mm, as shown by the figure, is mounted in place of the anode 29 and the graphite support 26.

The TiCl_4 was introduced by the distribution cavity 17 and by the series of tangential injectors 16 so as to impart a vortex motion in the zone of entry into the argon plasma.

The CH_4 was introduced by the radial injection tube 30', placed perpendicular to the axis of the furnace.

The TiC, obtained in a granulometry less than one micron, was found to be pure by X-ray examination, like the product obtained in example 3.

The operating conditions in this case were as follows:

Total current strength (at the primary arc and at the pilot arc)	121 amperes
Current strength at the pilot arc in the circuit 49	10 amperes
Arc voltage	170 volts
Total rated capacity (total power)	20.5 kW
Arc gas supply rate:	
Argon through inlet 9 of the classical head	1000 NI/h
TiCl_4 introduced by inlet 17	8.33 NI/h
CH_4 introduced by the inlet 30'	0.985 NI/h
Molecular ratio $\text{TiCl}_4/\text{CH}_4$	1.0
Hourly production of TiC:	2.5 kg/h
Theoretical conversion with respect to the supply of TiCl_4 and CH_4	95%

Energy consumption in kWh per kg of TiC	8.2 kWh/kg
Concentration of reacting substances (TiCl ₄ + CH ₄) in the injected plasma (A + TiCl ₄ + CH ₄):	
$\frac{0.985 + 0.985}{0.985 + 0.985 + 1.0} \cdot 100 =$	66.6% by volume
Argon consumption (Nm ³) per kg of TiC	0.4 Nm ³ /kg

After an uninterrupted period of operation of 1.5 hours, it was found that neither the electrodes nor other parts of the furnace had undergone corrosion or damage of any other kind.

The principal operating parameters and the results obtained in examples 1, 2, 3, 5 and 6 have been summarized in table 2 hereafter, showing the advantages which can be obtained with the method according to the invention, in the absence of hydrogen, as compared to the results obtained with the prior methods, as described in examples 1 and 2.

It is possible to obtain comparatively increased yields with the two reacting substances, in addition to the advantage of a lower gas consumption for the formation of the plasma and a low energy consumption per kg of product obtained.

Moreover, the commodious use of graphite as the primary anode material eliminates the risk of chemical corrosion effects.

Moreover, the powders produced often have better characteristics of resistance to oxidation, at least in the case of titanium carbide.

Furthermore, the method according to the invention can be used to prepare other products by carrying out reactions using halides of metals or of metallides.

In fact, these halides, when injected into the rare gas plasma, which is introduced at limited rates, very easily produce reactive fluid dynamic masses with a high thermal content and a strong concentration of reacting substances which, when injected in turn with other reacting substances, provide better conditions for the reaction to evolve in the desired direction.

Finally, the method according to the invention is able to prepare other ceramic and nonceramic products, as well as metallic and cermet products.

TABLE 1Oxidation of TiC in a current of oxygen

Type of product	Granulometry	Start of oxidation	End of oxidation	Increase in % by weight
TiC (carbo-thermal method)	$> 1/\mu$	400° C	910°C	33.2
TiC (argon-hydrogen plasma method)	$\sim 0.12/\mu$	300°C	470°C	29.5
TiC (argon plasma method)	$\sim 0.03/\mu$	390°C	900°C	15.5
Theoretical increase % = 33.2				

TABLE 2**Principal parameters of the method**

Example	1	2	3	5	6
Type of reactor	Classical with cooled anode	Per the method of the prior application	Per the method of the prior application	Per the method of the prior application	Per the method of the prior application
Magnetic field coil	None	of ordinary type	of ordinary type	of ordinary type	of ordinary type
Capacity in the plasma arc (kW)	45	15	15	15	20.5
Anode material	Cu (cooled)	W (graphite coating)	W (graphite coating)	W (graphite coating)	Graphite
Concentration of reacting substances in the injected plasma, % by volume	14.8	4.3	21.5	21.5	66,5
Molecular ratio $\text{TiCl}_4/\text{CH}_4$, %	1	1	1	1	1
TiC yield in relation to TiCl_4 , in %	51	98.8	-	-	-

TABLE 2 (continued)

Example No.	1	2	3	5	6
TiC yield in relation to CH ₄ , in %	51	98.8	-	-	95
Hourly flow rate of TiC in kg/h	1.39	0.472	-	-	2.5
Energy consumption per unit of product in kWh/kg of TiC	32.3	31.8	-	-	8.2
Consumption of hydrogen (as plasma-forming gas) per unit of product in Nm ³ /kg of TiC	8.45	14.00	0	0	0
Consumption of argon (as plasma-forming gas) per unit of product: Nm ³ /kg of TiC	0	2.75	-	-	0.4
Gas used to form the plasma	100% H ₂	16.55 % A 83.5 % H ₂	100 % A	100 % A	100 % A

TABLE 2 (continued)

Example No.	1	2	3	5	6
Ratio NI/h to kW between the gas used to form the plasma and the power applied to the arc	262	527	87	87	48.6
Possibility of using a graphite anode	no	no	specific	specific	specific
Resistance of a graphite anode	impossible	very bad	excellent	excellent	excellent

PATENT CLAIMS

1 - Plasma arc method for the production of powders of various chemical products from endothermal reactions, characterized in that it consists in carrying out, in a furnace with an anode function without dissipative cooling, operations consisting in forming a chemically reactive fluid dynamic mass with a high thermal content and a strong concentration of reactive substances, by injection into the electron column of the plasma arc of a rare gas, of at least one reacting substance chosen from among the halides of metals and of metallides that are injected with a mixing effect by a throttling injection and mixing nozzle, electrically insulated; bring about the electronic condensation of said mass inside an anode with a primary nozzle without dissipative cooling device; and, finally, injecting into said electronically condensed mass the remainder of said reacting substances that are necessary to accomplish what is considered to be the primary chemical reaction.

2 - Method per Claim 1, characterized in that the overall volume of the reacting substances is equal to or greater than 20% of the total aeriform volume formed by the total volume of the reactive substances correctly added to the volume of rare gas which pilots and stabilizes the plasma arc itself.

3 - Method per Claim 1 or 2, characterized in that the electronic condensation of said mass occurs inside a primary anode in the form of a nozzle without forced dissipative cooling, said nozzle-formed anode being either of tungsten or graphite.

4 - Method according to any one of Claims 1 to 3, characterized in that the electronic condensation of said mass is done in a primary anode in the form of a nozzle, preferably made of graphite.

5 - Method according to any one of Claims 1 to 4, characterized in that, in the final injection of one or more reacting substances into said fluid dynamic mass already electronically condensed inside the primary nozzle-shaped anode, one mixes, into one or more reacting substances, powders which play the role of nucleation and growth cores, that is, dispersion agents, and said powders may be chemically identical to or different from the product which the primary reaction is supposed to product.

6 - Method according to any one of Claims 1 to 5, characterized in that the powder produced by the primary chemical reaction is subjected, in the function of nucleation and growth cores for a composite material, to a subsequent reaction developed by the chemical and/or physical interaction of one or more reacting substances introduced into a zone of the furnace situated beneath the zone in which the primary reaction takes place.

7 - Method according to any one of Claims 1 to 6, characterized in that it consists, furthermore, in using hydrogen only as a reacting substance of the chemical reaction, said hydrogen being injected into the fluid dynamic mass after the latter has been electronically condensed inside the primary nozzle-shaped anode.

PLATE

